SYNOPSIS

“Development of Blended Polymeric Nano-composites for Device Applications”

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1) Introduction

Optoelectronic devices are electrical-to-optical or optical-to electrical transducers. Photodetector is one of the optoelectronic device which converts optical signals into notable electrical signals. Photo detectors are used as visible as well as invisible light sensors. Generally optoelectronic devices such as photo detectors, phototransistors, photodiodes are based on metal oxide, metal sulfide thin films. Oxide materials in bulk and thin film form, and metal oxide nanostructures exhibit a great variety of functional properties which make them ideal for applications in solar cells, gas sensors, optoelectronic devices, passive optics, catalysis, corrosion protection, environmental protection, etc.

Metal oxide's functional properties are strongly dependent on oxide's crystal structure, composition, native defects, doping, etc., which govern their optical, electrical, chemical and mechanical characteristics. Processing methods and growth parameters strongly determine the morpho-structural characteristics and therefore the physico-chemical properties of metal oxides. The band gap and electronic structure of oxides can be controlled by the size and dimension, resulting in a wide range of potential applications.

Metal oxide thin films are used in solar cells and optoelectronic devices; transparent conductive oxides (TCOs); plasmonics; photonic integrated circuits; chemical sensors; catalysis; corrosion protection; thermal protection; and energy conversion and storage. The mechanical Flexibility of metal oxides is very less. Photo detectors based on metal oxides or metal sulfides, have some sensing limitations in case of mechanical flexibility.

Recent work is based on the synthesis and development of non-metallic composite, blended polymers which are flexible as well as conducting. Instead of traditional metal oxides if we want to use flexible material thin films then we can think for polymers and its composites which has high mechanical flexibility. Generally polymers are insulators but there are certain polymers which has high electrical conductivity.

Conductivity of polymers is due to conjugation (alternate single-double bond existence) or it is due to doping. The Doped conducting polymers such as Poly Aniline (PANI) ,Poly(Thiophene) , Poly(ethylenedioxythiopene)PEDOT has good electrical conductivity. The photo detectors based on Poly Aniline thin films are the devices with mechanical flexibility , has low cost & are light weight , Used in flexible image sensing , photodetectors, surveillance and health monitoring, Printed Circuit Boards(PCB), Organic Light Emitting Diodes(OLED), different sensors.

Poly aniline (PANI) is known as a good electricity conducting polymer. When Aniline($C_6H_5NH_2$) also known as amino benzene undergoes Partial Oxidation gives Leucomeraldine (C_6H_5NH), which is ,white colored/clear poor electricity conductor. Aniline($C_6H_5NH_2$) after complete oxidation gives , Emeraldine (C_6H_5NH) which is conducting, green colored for salt and blue coloured for base material. There are three types of PANI based on oxidation states A) Leucomeraldine(Fully reduced) B)

Pernigraniline(Fully Oxidized) and C) Emeraldine (Partially Oxidized) [1]. Emeraldine is a good conductor as compared with rest of two. In our recent work we are going to use Emeraldine as base material and after making its different nano composites. After making thin films based on Conducting PANI we may take its IV characteristics, Fourier Transform Infrared Spectroscopy (FTIR) analysis ,X-ray Diffraction XRD, viscosity, carbon Nuclear Magnetic Resonance (NMR)/Proton NMR ,UV-Vis spectroscopy, Raman spectroscopy, Thermo gravimetric Analysis –Differential Thermal Analysis(TGA-DTA), Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS), X-ray Photoelectron spectroscopy(XPS), etc.

To study the electrical conductivity and carrier mobility, of polymer thin films properties of polymer thin films and nanostructures using dedicated electrical characterization

setup. we may get good conductivity, good optical /photo response and different exciting results. The possible conducting polymers that can be used for the work are as shown in the figure below.

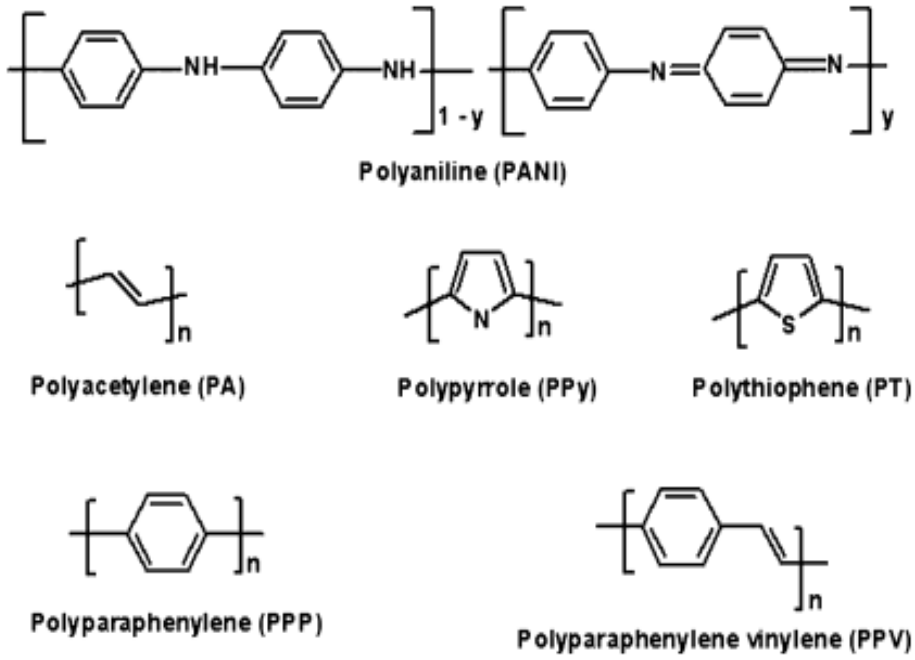

Fig. 1. The structure of a number of intrinsically conducting polymers (ICP).

2. Review of Literature and Development in the Subject:

Optoelectronic devices transform electrical signals into optical signals and vice versa by utilizing the sophisticated interaction of electrons and light within micro- and nano-scale semiconductor structures. In recent years there has been a growing interest in flexible optoelectronic devices such as: liquid crystal displays (LCD), solar cell panels and organic light emitting displays (OLED) [1-4]. Many advantages are

obtained when these devices are made conformable so that they are portable and can be rolled. For example one possible application is to cover the roof of a building with flexible solar cells, which would be difficult with rigid ones. Because of their low cost, lightweight and mechanical flexibility, polymeric films are often used as the substrate in such devices to carry the active coatings [5].

3. Objectives of Research/ Proposed Hypothesis:

This work proposes efficient method for synthesis of Blended polymeric nano composites for device applications. Optoelectronic devices are electrical-to-optical or optical-to-electrical transducers. Photodetector is one of the optoelectronic device which converts optical signals into notable electrical signals. Photo detectors are used as visible as well as invisible light sensors. Generally optoelectronic devices such as photo detectors, phototransistors, photodiodes are based on metal oxide, metal sulfide thin films. Photo detectors based on metal oxides or metal sulfides, have some sensing limitations in case of mechanical flexibility. In Recent work we are trying to get the synthesis and development of non-metallic semiconductors based on composit , blended polymers which are flexible as well as conducting. Instead of these materials if we want to use flexible material thin films then we can think for polymers and its composites which has high mechanical flexibility The basic concept of photodetectors is that it converts optical radiation to electrical radiation using different materials. Different Metal oxides are used for device applications but they are mechanically less flexible so we can use conducting polymeric blended nanocomposite of different materials for mechanical flexibility .

This work will investigate device properties of Blended polymeric thin films synthesized using various techniques. To achieve the above mentioned objective this work is made of
specific aims

a. To synthesize Blended polymeric thin film and nanostructure on substrate using different techniques.
b. To characterize synthesized thin films and nanostructure using XRD, UV-Vis Spectroscopy, Raman spectroscopy, FTIR, TGA-DTA, SEM-EDS, NMR, XPS, etc.
c. To study the electrical conductivity and carrier mobility, of polymer thin films Properties of polymer thin films and nanostructures using dedicated electrical characterization
setup.
c. To probe the electronic structure of the film using X-ray photoelectron spectroscopy and understanding the role of its intrinsic properties on charge transport.
d. To propose effective device based on the results and material properties.

4. Methodology to be adopted:

The work predicted under this plan involves efforts on several different aspects and their
integration in the interest of a desired property response and/or device action. The work elements can be broadly categorized under four classes namely materials synthesis, film growth, processing and characterization, although the processing and growth aspects could be employed interchangeably depending on the nature of the desired film. In terms of a plan definition, the following activities/effort elements can be presented, however, the specificity could evolve dynamically depending on the success or failure of a particular approach and the need to modify or steer the same.

Activity 1: Employing physical / chemical / electrical methods for synthesis of blended polymeric nanostructuredmaterial of interest:

This will involve synthesis of blended Polymeric material (undoped and
doped polymer nano composites) via physical or chemical routes with various specifications. In this domain the in-house efforts will be complimented and enriched to synthesize polymer.

Activity 2: Post processing of the nano-structured material:

The next step will be to achieve physico-chemical integration of the nanosystems and the underlying film configuration, to generate a new/novel response specific to the hybrid aspect of the coupled system. This may involve low temperature annealing/sintering, radiation sintering or overgrowth to embed the self assembled structure.

Activity 3: Characterization:

Employing a broad based characterization manifold is key to both, the process parameter optimization for the growth of specific configurations andelucidation of the property features realized in such hybrids. It will of course be important to separately characterize the films and the nano systems for their quality and property optimization. The characterization techniques which will be liberally employed will include xray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), optical spectroscopy, Raman spectroscopy, x-ray photoelectron spectroscopy (XPS),Nuclear Magnetic Resonance (NMR) etc.

Activity 4: Device actions explorations:

The device action categories for which the nano-film hybrids will be examined include the Reponsivity, electrical resistivity, thermal conductivity and thermoelectric properties of polymers. Synthesis of polyaniline by Chemical oxidation/Reduction Method is shownbelow.[4]

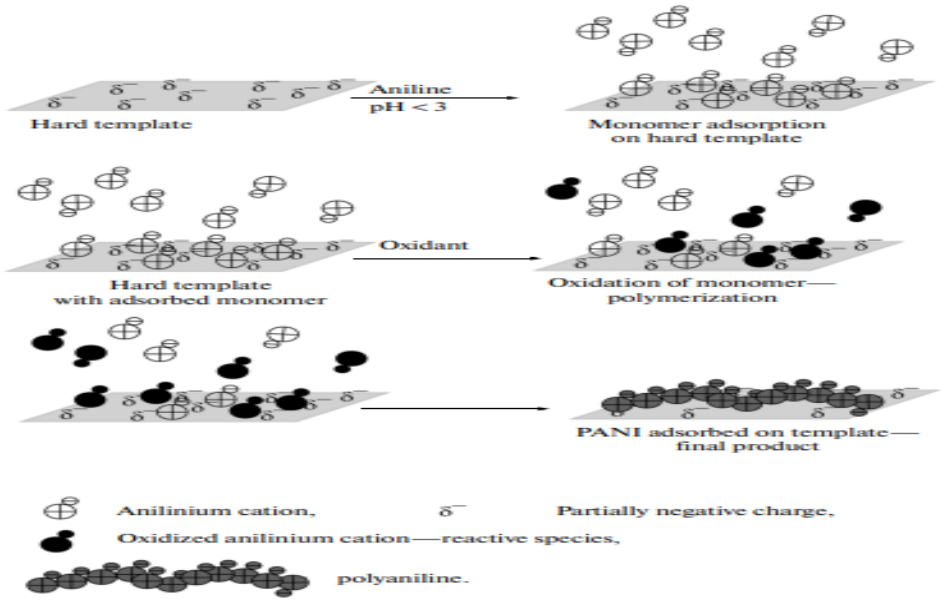

Fig.2 Synthesis of polyaniline

5. Importance of study/ Society applications:

National Status

Sambhu Bhadra, Dipak Khastgir ,Nikhil K. Singhaa, et al have done work on PANI and they that PANI can be prepared using different techniques. The resultant product can be converted to fine powder, fiber to nanofiber, thin film, etc. The properties of PANI also depend on the method of preparation. PANI is a heterogeneous system consisting of a partly crystalline region (ordered) and an amorphous region (disordered region). The crystalline domains are metallic in nature, where conduction occurs . These metallic grains are surrounded by an amorphous region that has disordered or folded chains which reduce the conductivity of PANI. The conductivity of PANI depends on molecular weight, oxidation level, molecular arrangement, percentage crystallinity, inter-chain separation and degree of doping. The conductivity and processability of PANI can be improved by using various types of dopants. The limitation of the processability of PANI can also be overcome by using it as conducting filler in composites. These types of composites can be processed easily, show good mechanical properties and have numerous applications. PANI can be applied in different areas such as electrical, electronics, thermoelectric, electrochemical, electromagnetic, electromechanical, electro-luminescence, electrorheological, chemical, membrane, sensors, and so on.

Surajit Sinha, Sambhu Bhadra, Dipak Khastgir et al have Studied different type of dopants on the properties of polyaniline (PANI) is relative less although dopant has profound effect of the properties of PANI. effect of different type of dopant, namely strong inorganic hydrochloric acid (HCl), organic and aromatic acids containing different aromatic substitution, namely *p*-toluene sulfonic acid (PTSA),

dodecylbenzenesulfonic acid (DBSA), organic and aliphatic acids having long hydrocarbon chain, namely lauric acid (LA), on the properties of PANI. The PANI was prepared through oxidative polymerization methods and doped with HCl, PTSA, DBSA, and LA and then characterized through different methods like conductivity measurement, UV, X-ray, DSC, TGA, and SEM. It was found that the properties of doped PANI depend on the type and molecular size of the dopant. With the increase in dopant chain length, the crystallinity is decreased, whereas the *d*-spacing, interchain separation, and solubility are increased. The bond formation of water molecules with the backbone nitrogen of the polymers is much less in presence of aromatic dopants when compared with those of inorganic or aliphatic dopants. [6]

Interntionl Status:

Ali Eftekhari, Lei Li , Yang Yang et al have studied conducting properties of polyaniline and found that Polyaniline (PANI) has been widely used for the energy storage applications [6] either as a conducting agent or directly as an electroactive material due to the tunable pseudocapacitive performance. Polyaniline can be doped with metal oxides to form nanocomposites for various energy applications and for various sensing applications.

Kwanghee Lee, Shinuk Cho , Sung Heum Park , A. J. Heeger , Chan-Woo Lee & Suck-Hyun Lee et al have studied polyaniline & found that conducting properties of some polymers like PANI are same as that of semiconductors[5] . The low-temperature behaviour of 'metallic' polymers has, in all previous cases, exhibited an increase in resistivity as temperature is further decreased, as a result of disorder-induced localization of the charge carriers. This disorder-induced localization also changes the infrared response.

A.JEpstein, J.MGinder , FZuoR., WBigelowH.-SWooD.BTannerA.FRichterW.-SHuangA.G et al have studied on polyaniline and found that The emeraldine base (EB) form of polyaniline can be varied from insulating ($\sigma < 10^{-10}$ohm^{-1}cm^{-1}) to conducting ($\sigma \approx 10^{+1}$ohm^{-}cm^{-}) through protonation. That is, the number of electrons on the polymer backbone is constant while the number of protons is increased. They found that resulting emeraldine salt (ES) is metallic with a finite density of states at the Fermi energy base on magnetic, optical and transport data. The results are consistent with segregation into fully protonated emeraldine salt and unprotonated emeraldine base polymer regions. it is proposed that the observed transition is an isolated bipolaron-to-polaron lattice transition.[8]

A.c.macderamid et al have studied on The analytically pure base form of polyaniline, , corresponding to the emeraldine oxidation state is converted from an insulator ($\sigma \sim 10^{-10}$S/cm) to a metal ($\sigma \sim 5$ S/cm) by treatment with ~ 1M aqueous HCl

to form the corresponding salt, emeraldine hydrochloride. This involves a new type of doping of a conducting polymer in that the number of electrons associated with the polymer undergoes no change during the protonic acid doping process. The metallic emeraldine hydrochloride is believed to be a delocalized poly(semiquinone radical cation) having a polaron conduction band, with most of the positive charge residing on the nitrogen atoms. It exhibits a finite density of states at the Fermi energy.[9]

Significance of the study:

As stated earlier, this work aims to make a modest contribution to the highly desirable goal of being able to bridge the wide gap between existing optoelectronic devices based on metal oxides and modern devices based on blended polymeric nano composites , especially in the high technology domain. It focuses on the issue of metal oxides based mechanically non flexible, hard , high cost containing devices to large processing area based materials. This platform emphasizes synergetic integration with potential for novel effects exclusive to the hybrid concept for blended polymeric nanocomposite materials.

6. Proposed work Plan/Formation and Structure of Study: Year-wise Plan of work and targets to be achieved:

First Year:

a. To Initiate synthesis of undoped polymer thin films and nanostructures using oxidation/Reduction method
b. To Initiate and optimize different preparation techniques of Polyaniline(PANI) .
c. Study effect of temperature on film morphology.
d. Perform extensive in-house characterizations including UV-Vis, XRD, AFM, TGA, etc. as well as those involving external collaborations SEM-EDS, TEM and XPS to know the structural, optical, thermal and electronic properties of synthesized thin film.

Second Year:

a. Establish and implement characterization strategies for the films and the nanofilm hybrids.
b.To Initiate testing of device properties of undoped polymer films.
c. To Initiate and optimize Chemical Oxidation/Reduction technique for doping of functional polymers.

Third Year:

a. To Perform extensive in-house characterizations including UV-Vis, XRD, AFM, TGA, etc. as well as those involving external collaborations SEM-EDS, TEM and XPS to know the structural, optical and electronic properties of synthesized thin film.
b. To Test of device properties of doped Blended polymeric nanocomposite films.
c. To Start publishing research papers.

Fourth Year:
a. To Review the status of progress during the first two years and to take appropriate steps towards the most effective utilization of the knowledge, facilities and experience during the remaining duration.
b. To Continue to analyze the data obtained and proceed with publications/patenting as appropriate.
c. To Conduct meetings with industry and national laboratory personnel to explore application avenues.
d. Preparation of thesis for submission.

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